

WETTABILITY OF PETROLEUM COKES BY PITCH

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In 1968 well over a million tons of petroleum coke were used in the United States in manufacturing carbon and graphite. For carbon anodes in aluminum smelting, delayed petroleum coke mixed with coke-oven pitch and subsequently baked has been used almost exclusively. While many investigations have been made on the properties required in binder pitches for carbon electrodes (1), there are no data on the characteristics of cokes other than impurity content and real density that relate to anode properties.

Microstructures of a variety of cokes and carbons were reported by Martin and Shea (2). In a petroleum coke, Kusakin et al, 1965 (3), observed two different types of particles: "spherulitic" particles, which are isotropic and relatively non-graphitizing, and a "streak" type, which is softer and graphitizing. Abramski and Mackowsky have developed methods for measuring in the microscope characteristic parameters for coke pores and walls (4). Other coke properties such as microporosity, macroporosity, and surface area have been measured. Rhedey (5) obtained a correlation between aggregate porosity and binder requirement of Soderberg paste for constant flowability. However, in none of the work is a correlation shown with baked anode properties.

A measurement related to porosity but more useful in assessing the effect of widely different calcined cokes on Soderberg anodes is the "wettability" by pitch. For the investigation reported here, an empirical procedure for measuring wettability was adapted from the elongation test used by Bowitz et al (6).

Procedure

In the modified elongation test, a mixture of 100 g -140 +200 mesh (Tyler) calcined coke and 120 g standard pitch (softening point 110°C, cube-in-air) was stirred in a small can at 160°C for 20 minutes with a spatula. Cylindrical specimens 45-50 mm long and 9 mm diameter were molded and cooled. The specimens were placed on the inclined board in an oven at 160°C for one hour. After cooling, the change in length (elongation) of the specimen was measured and the percent elongation calculated. The less an aggregate was wet by the standard pitch used in these tests, the greater was the elongation. The increased elongation was caused by the greater amount of pitch available in the space between coke particles because of decreased absorption into the pores.

Real densities were determined using a pycnometer with kerosene as the confining fluid (Alcoa Analytical Procedure 424). Microporosity was calculated as 100 times the difference between real density and the density with mercury as the confining fluid divided by the real density.

Samples were mounted for microscopic observation by impregnating at 29 in. Hg vacuum with Maraglas Type A resin and Maraglas hardener 555 (7). After standing overnight, samples were cured at 70°C for 16

hours. They were ground successively on 320, 2/0 and 4/0 grit papers on a glass plate, polished on a wheel with Metaui 6 mu (Euhler, Ltd.), with alpha alumina, and finally with gamma alumina.

For preparing baked anodes, an aggregate particle size distribution was used having the greatest dry bulk density as determined in a series of settling experiments on a vibrating table. Cokes G and W were used as 46.5 percent of the total aggregate in the coarse fraction without crushing. The sizing of coke P was then adjusted for maximum dry bulk density of the blend. Similarly, coke A was used in the fines, as received, and the sizing of coke P was adjusted for maximum dry bulk density. Anodes were made with about 27 percent pitch (softening point 105°C cube-in-air). The amount of pitch was adjusted so that all mixes had the same elongation as determined on a specimen 2-1/2 in. long x 1 in. diameter molded from the green paste. Anodes 3 in. diameter x 4 in. tall were baked to 1000°C under 3.7 psi pressure. Baked apparent density (EAD) and electrical resistivity were determined on the baked samples.

Results

The elongation test procedure of Bowitz et al (6) specified 80 percent coke passing through a 200 mesh sieve. Lack of a lower limit permitted a wide range in particle size and surface area of the sample. In addition, the fine grinding could destroy much of the pore volume. Preliminary tests demonstrated greater reproducibility when using five fractions between 100 and 325 mesh (Tyler). The sizing finally chosen, -140 +200 mesh, gave even better reproducibility. To increase ability of the test to discriminate among cokes, the pitch content was increased to 54.5 percent. Typical results are shown in Table 1 for two successive mixes of coke P, with 18 specimens molded from each mix and tested in the oven, six at a time.

Table 1

Reproducibility of Elongation Test for Coke P

| Test | Elongation, % | | | | | |
|-------------------|---------------|------|------|-------|------|------|
| | Mix 1 | | | Mix 2 | | |
| | 1 | 2 | 3 | 1 | 2 | 3 |
| | 60.0 | 56.0 | 63.8 | 64.2 | 61.5 | 56.7 |
| | 58.1 | 57.6 | 63.2 | 64.0 | 64.3 | 59.3 |
| | 56.9 | 55.4 | 63.2 | 66.1 | 61.8 | 60.1 |
| | 53.4 | 54.0 | 60.1 | 61.9 | 59.5 | 62.2 |
| | 53.8 | 61.2 | - | 68.3 | 64.5 | 58.7 |
| | 61.2 | 58.7 | - | 63.7 | 65.8 | 64.7 |
| Average | 57.2 | 57.2 | 62.6 | 64.7 | 62.9 | 60.3 |
| Std. deviation | 3.99 | 2.58 | 1.66 | 2.21 | 2.35 | 2.34 |
| Average for Mix 1 | 58.5% | | | | | |
| Average for Mix 2 | 62.6% | | | | | |

For the particle size chosen, -140 +200 mesh, the accessible porosity appeared completely filled with pitch because increasing mixing temperature to 200°C and 230°C did not change the amount of elongation. However, the degree to which pores in larger particles were penetrated by pitch was affected by mixing temperature. For example, with a typical anode aggregate (-4 mesh +pan) molded into 1-in.

diameter 2-in. long cylinders there was a marked decrease in elongation with increased mixing temperature (Figure 1). At the lower mixing temperature, viscosity of the pitch prevented substantial penetration into the remote pores of the larger particles.

Three calcined delayed cokes had elongations from 61 to 227 percent (Table 2), and the calcined fluid coke had an elongation of 355 percent. Anode properties, as measured by baked density and resistivity, varied with elongation and seemed to optimize at the intermediate values of 186 and 227 percent. Anode properties did not correlate with real density or the microporosity measurement of the calcined cokes.

Table 2

Properties of Calcined Cokes and Laboratory Anodes
Made from Mixtures with Coke P in the Aggregate

| Coke | P | G | W | F |
|----------------------------------|---------|---------|---------|-------|
| Process | Delayed | Delayed | Delayed | Fluid |
| Real Density | 2.02 | 1.96 | 2.03 | 1.98 |
| Microporosity | 10.9 | 8.2 | 13.3 | 3.5 |
| Elongation, % | 61 | 186 | 227 | 355 |
| <u>Anode Properties</u> | | | | |
| Amount of Coke P in Aggregate | 100 | 53.5 | 53.5 | 57.5 |
| Baked app. density | 1.39 | 1.44 | 1.43 | 1.41 |
| ρ , ohm-in. | .0028 | .0025 | .0025 | .0032 |

Microscopic examination showed that green delayed petroleum coke (Figure 2) had the incipient pore structure of calcined coke (Figure 3). In green coke the pores were filled, probably with a hardened residuum from the coker feed, which distilled off during calcination and exposed the pores and typical lamellar structure of calcined coke.

Although cokes P, G, and W were made by the delayed coking process, each had a distinctive microstructure. Coke P (Figure 3) had the lamellar and pore structure typical of many delayed cokes. Coke W (Figure 4) had in addition a characteristic mottled structure. Coke G (Figure 5) consisted of fused spherules, each having an onion-like structure. Each spherule had a microporous surface coating.

The fluid Coke F (Figure 6) consisted of spherical particles, each in turn frequently being made up of clusters of small spherules of isotropic coke. Some of the larger particles had the onion-like structure.

Discussion

The wide range of microstructures indicates the difficulty in trying to find a single characterization factor for cokes in carbon anodes. The wettability test, however, largely overcomes this objection since it is a direct measure of how the pore structure affects the relationship between coke and binder. For example, the fluid coke

F, with its limited amount of surface accessible pores had poor wettability as judged by elongation. Because of the poor bond between coke and binder, fluid coke produced anodes with high resistivity. This poor bond in anodes was clearly discernible in the microscope (Figure 7). Attempts were made to alter the surface of Coke F to improve the bond with binder pitch. Neither crushing to expose fresh surface nor chemical etching with oxygen was successful (Table 3).

Table 3

Effect of Treatment of Coke F on Properties of
Anodes Containing 20% of Coke F

| <u>Treatment</u> | <u>Baked App. Density</u> | <u>Resistivity ohm-in.</u> |
|------------------------------------|-------------------------------|--------------------------------|
| Untreated | 1.41 | .0029 |
| Crushed to -100 mesh | 1.40 | .0030 |
| Oxidized at 1050° to 6% wt loss | 1.38 | .0031 |

This was consistent with the explanation that pores in the aggregate accessible to the binder are necessary to produce a good bond. After coking of the binder, the binder coke and aggregate coke are kept from separating by the mechanical action of binder coke formed within the pore system of the aggregate. Coke G formed an excellent bond with the binder coke (Figure 8), probably because the binder was able to penetrate the porous layer characteristically on the surface of this coke (Figure 4).

Because coke P had a high wettability by binder, the green mix required a high pitch content, and this may have been a factor in the high resistivity. The large pores and laminations in Coke P may also have contributed to the high resistivity by presenting a tortuous path for current flow.

The cause of differences in microstructure of the delayed cokes is not known. Since all were made by the same process, operating variables such as recycle ratio could be a factor. The presence of nuclei seems to favor isotropic coke. For example, needle coke, a non-isotropic coke is made by a 2-step process in which the nuclei present in the feed stock are first removed and the needle coke is prepared from the clarified feed (8). Even more important for Coke G may be the chemical nature of the feed to the delayed coker. It has been reported (9,10) that heterocyclic structures tend to produce isotropic cokes and the feed for Coke G had a relatively high nitrogen content.

For carbon manufacture the wettability test can be used to predict behavior in anodes of cokes having a wide variety of microstructures. Low wettability indicates a poor bond may be expected between baked binder and coke, and this will cause high electrical resistivity. On the other extreme, high wettability may indicate an extremely porous coke whose interior pores unfilled with binder can cause high electrical resistivity.

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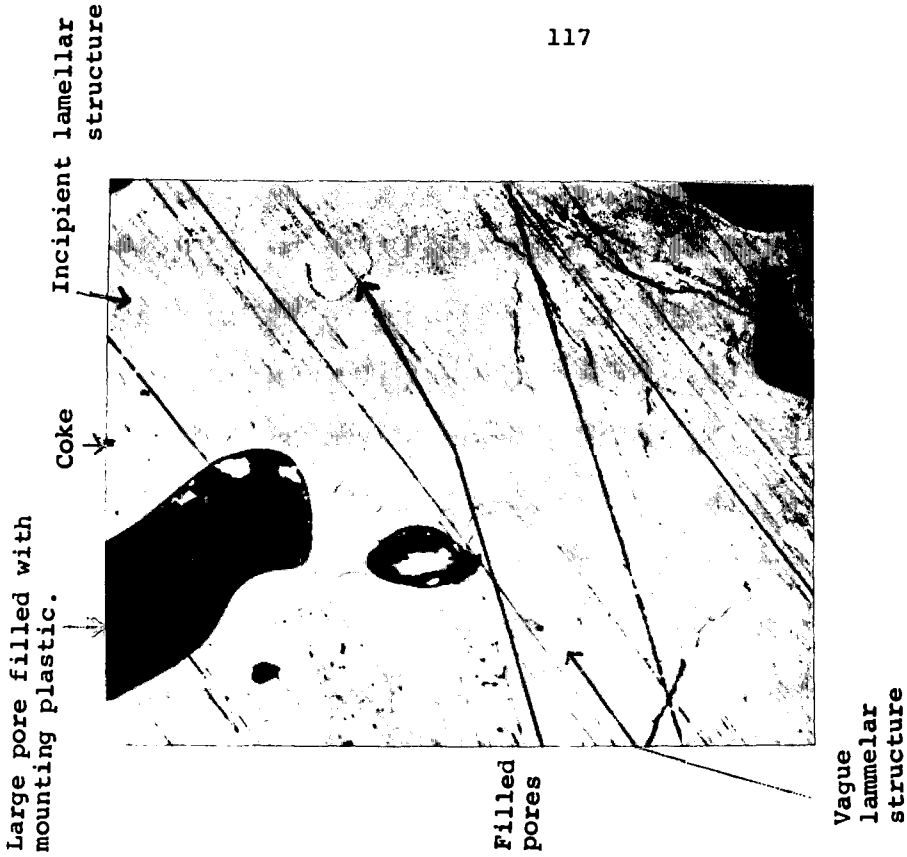
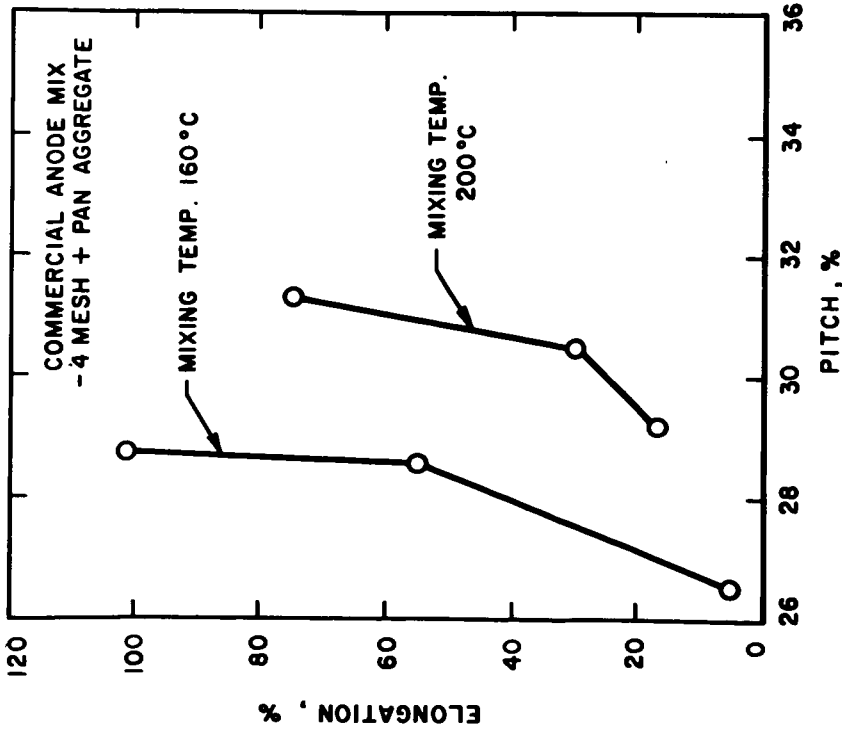


Figure 2
Green Delayed Coke P
100X



EFFECT OF MIXING TEMPERATURE
ON ELONGATION

FIG. 1

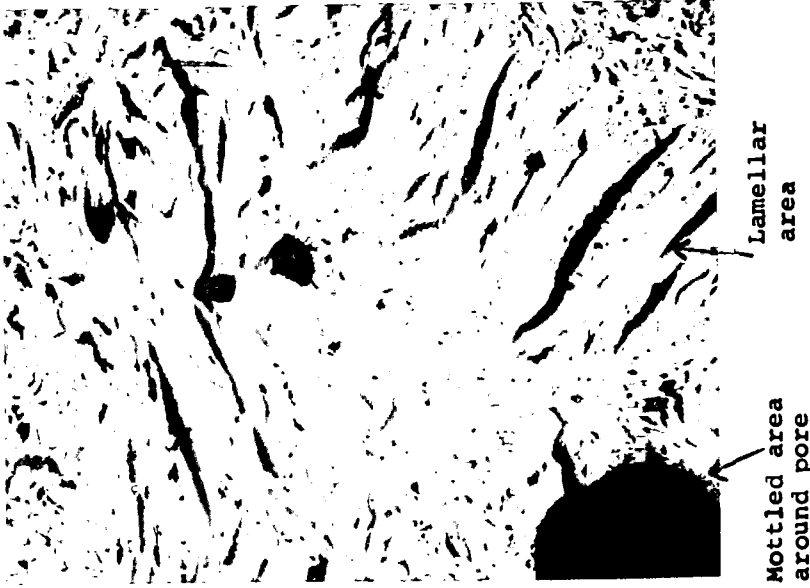


Figure 4
Calcined Delayed Coke W
100X

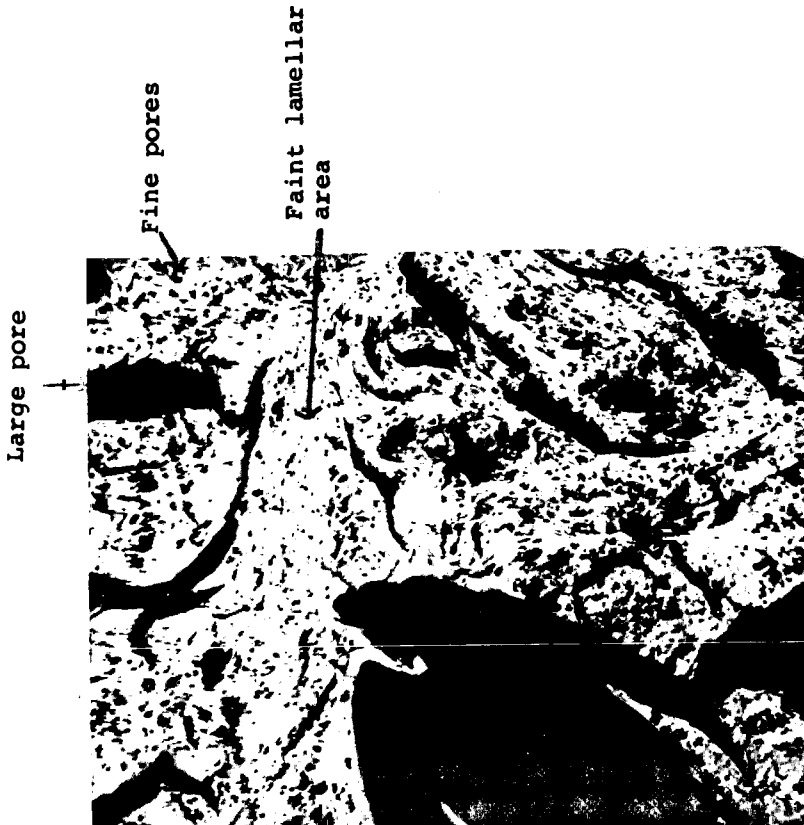


Figure 3
Calcined Delayed Coke P
100X

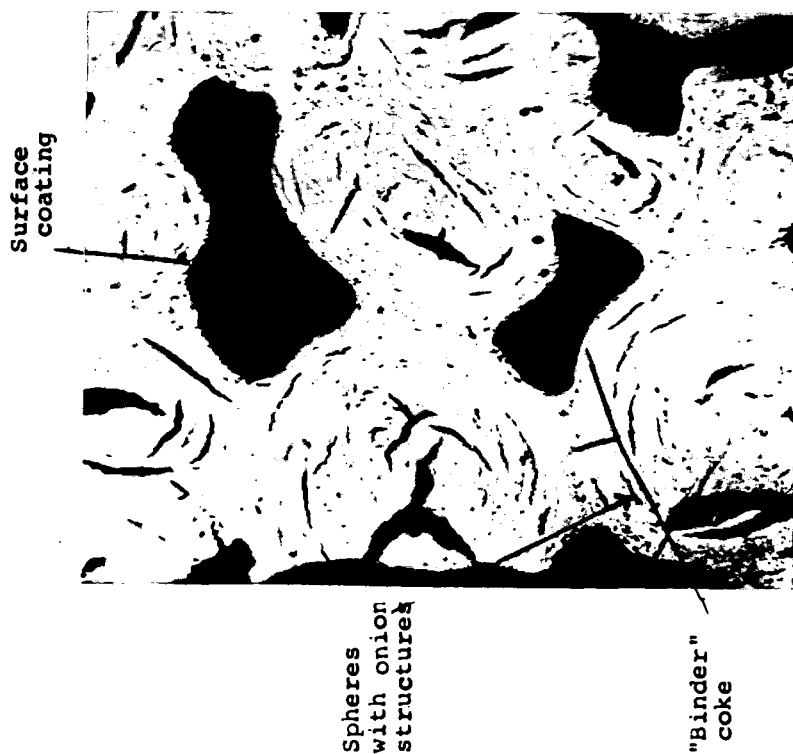


Figure 5
Calcined Delayed Coke G
100X

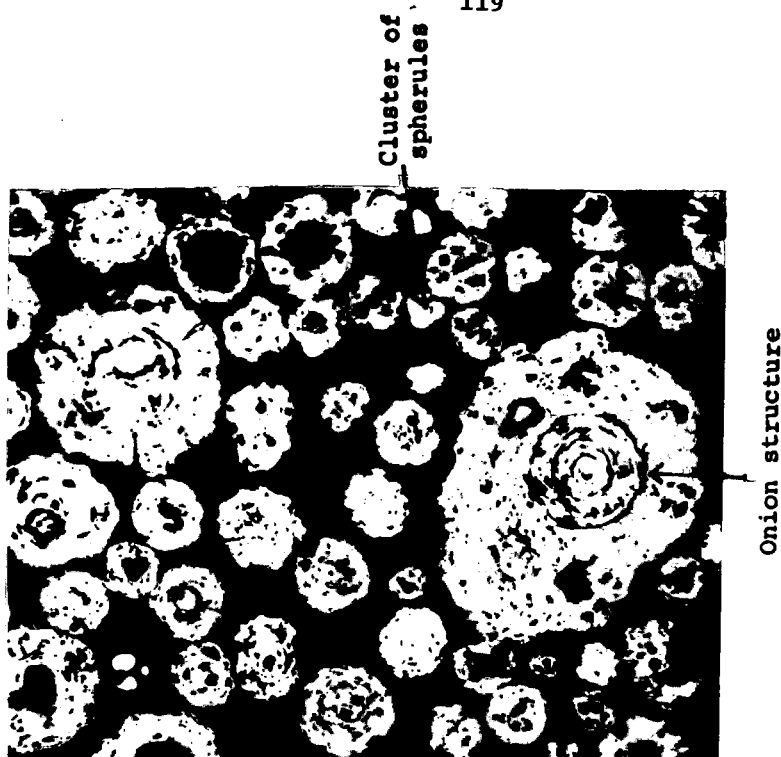


Figure 6
Fluid Coke F Baked in Laboratory
100X

Separation between Coke F and binder

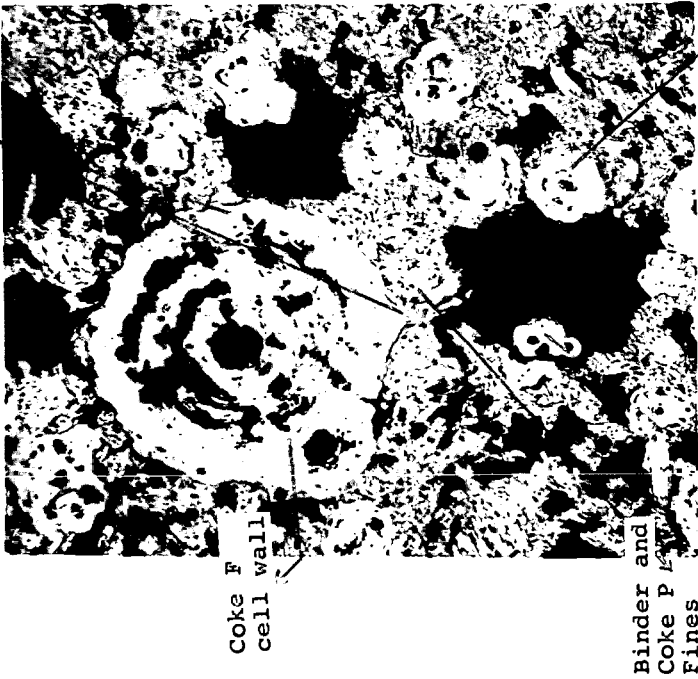


Figure 7 - Laboratory Soderberg Anode Containing 20% Coke F (100X)



Figure 8 - Laboratory Soderberg Anode Containing 46-1/2% of Coke G (100C)